Towards a 32-electron principle: $Pu@Pb_{12}$ and related systems[1]

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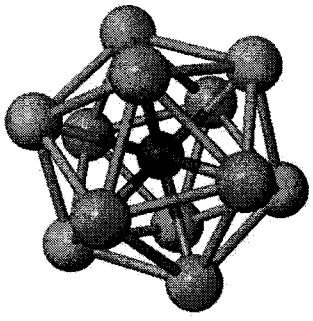
The 18-electron principle goes back to Langmuir.[2] For its history and interpretation, see the recent paper.[3] Formally it would correspond to fully occupying at a central atom its ns, np and (n-1)d orbitals. For early 5f-elements the f-shell becomes chemically available and remains so until about Am. Theoretically it could be filled with 14 further electrons, bringing the total to 32, a theoretical possibility already evoked by Langmuir.[2] How far towards that limit can one go? Thorocene, $Th(C_8H_8)_2$, was classified as a '20e' case.[3] In the 'metalloactinyl' compounds, like the linear $IrThIr^{2-}$, one could potentially reach '24e'.[4]

We now find that the 6p valence band of the recently discovered icosahedral $[Pb_{12}]^{2-}$ shells forms a perfect partner for the 5f shell of an enclosed actinide atom, like plutonium. Detailed DFT calculations suggest that the system is viable. It could be on good grounds characterised as a '32e' system.
The calculated molecular geometries, an orbital analysis and a bonding energy analysis in term of Morokuma-type decomposition will be presented for $[Pb_{12}]^{2-}$ and $[M@Pb_{12}]^{x-}$ with M=Yb, Th, U, Np, Pu, Am, Cm. The orbital-energy spectra and the densities of states for $[Pb_{12}]^{2-}$, $[An@Pb_{12}]^{x-}$ (An=Pu, Am, Cm) will be given. Finally we will show for $[Pu@Pb_{12}]$ an ELF distribution, clearly demonstrating the radial bonds.



[1] J.-P. Dognon, C. Clavaguéra, P. Pyykkö, *Angew. Chem. Int. Ed.* **2007**, *46*, 1-5
[2] I. Langmuir, *Science* **1921**, *54*, 59-67,this paper mentions the 8, 18 and 32-electron closed shells and uses on pp. 65-66 $Fe(CO)_5$, $Ni(CO)_4$ and $Mo(CO)_6$ as examples on 18e.
[3] P. Pyykkö, *J. Organomet. Chem.* **2006**, *691*, 4336-4340
[4] P. Hrobárik, M. Straka, P. Pyykkö, *Chem. Phys. Lett.* **2006**, *431*, 6-12